New Developments in Nanotube / Polymer Composites

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Abstract

Multiwall nanotubes (MWNT) have been in commercial use as a conductive additive for engineering resins, such as polycarbonate and nylon, since the early 1990's. Recently, they have been used in thermosetting fluoroelastomers used to make O-rings for automotive fuel line connectors. In addition, two groups have recently showed that multiwall carbon nanotubes may act as a non-halogenated flame retardant. This presentation will review these new developments.

Characterization of Multiwall Nanotubes

Carbon multiwall nanotubes were first synthesized in 1983 by scientists at Hyperion Catalysis International. These nanotubes are approximately 10 nanometers in diameter and 10 microns long. They are made by a continuous, catalyzed, high temperature gas phase reaction. Figure 1 is a representation of the graphitic multiwall structure

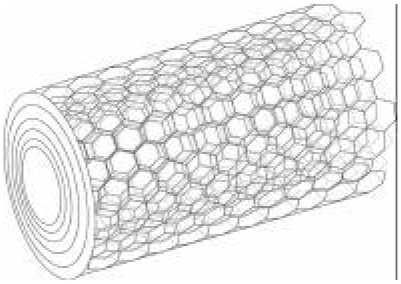


Figure 1. Graphic of MWNT

Figure 2 is a transmission electron microscope image of a portion of a nanotube showing the multiwall structure surrounding the hollow core.

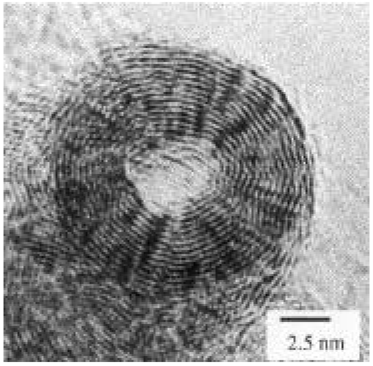


Figure 2. TEM end-on view of a MWNT

Figure 3 is a scanning electron microscope image showing the curvilinear structure of multiwall nanotubes.

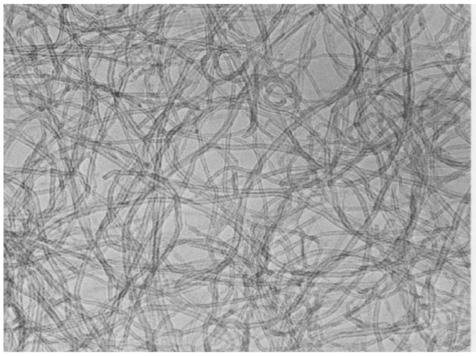


Figure 3. SEM of MWNT

Carbon nanotubes have proven to be an excellent additive to impart electrical conductivity in plastics. Their high aspect ratio (length divided by diameter) of 1000 means that a very low loading is needed to form a percolating mixture in a polymer compared to materials with lower aspect ratios, such as carbon black, chopped carbon fiber, or stainless steel fiber, see Figures 4 and 5.

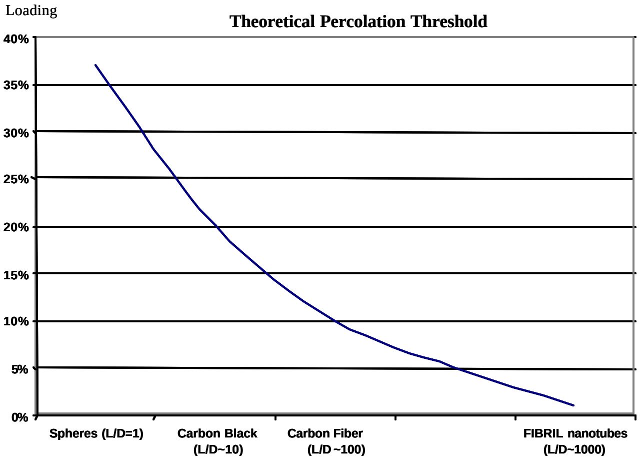


Figure 4. Effect of aspect ratio on percolation threshold loading

Performance of Carbon Nanotubes as a Conductive Additive for Elastomers

The advantages of MWNT in traditional engineering resins such as polycarbonate and nylon have been reviewed at previous Nanocomposites conferences. The use of a low loading of a very small nanotube as a conductive additive gives greater retention of the base resin's toughness. This is important in automotive applications like fuel system components or exterior body panels that must be static dissipative but must also be able to withstand low temperature impacts without a catastrophic failure. For the electronics industry, the low loading of a very small nanotube gives a static dissipative part with a smooth surface that has much lower particulate sloughing. Particulates and static are VBT (very bad things) in the manufacture of computer hard disc drives or in the manufacture of computer chips.

Recent work by Hyperion has shown that certain classes of what is typically thought of as a thermosetting elastomer can be compounded with our nanotubes to make a masterbatch. This masterbatch can then be let down and curing agents added to make a conductive elastomer.

The principle advantage of these thermosetting elastomers is that they have better chemical resistance and a lower durometer (durometer is a measure of surface hardness) than thermoplastic elastomers. O-rings for quick-connectors used in automotive fuel lines have a need for chemical resistance, low permeability to minimize evaporative losses and low durometer for good sealing and low insertion force. They are frequently made from a class of fluoroelastomers called FKMs (DuPont's VITON® fluoroelastomer is one example).

There is a growing mandate from the car manufacturers for a continuous conductive pathway in the fuel system from fuel tank to engine. Even if the fuel lines and the connectors on each end of the fuel line are conductive, an insulating O-ring will break the conductive pathway and possibly allow the accumulation of a static charge. Up until recently the issue has been that to make an O-ring conductive with carbon black involved unacceptable sacrifices in the part's performance.

Recently Precix Inc., a major manufacturer of sealing systems for automotive, aircraft and industrial uses, has developed a nanotube-based conductive O-ring for automotive quick connects. Table 1 compares properties of the nanotube-based product with the carbon black-filled product. It is clear that the nanotube-based formulation has a comparable elongation and a much lower durometer. This gives a better seal with lower insertion force.

Table 1. Comparison of Durometer and Elongation

Additive	Shore A Durometer	Elongation %
Nanotubes	79	>200
Carbon black	86	>200

In order to perform correctly, an O-ring should have good dimensional stability under the conditions of use. Table 2 compares the change in volume of the two formulations after exposure to two different gasoline formulations.

Table 2. Swell Upon Exposure to Fuel for 70 hrs. @ Room Temperature

Additive	100% Fuel C % vol. change	85% Fuel C / 15% Methanol % vol. change
Nanotubes	+2.7	+11.3
Carbon black	+8.6	+17.7

Of particular interest is the improved resistance of the O–ring to gasoline permeation. Automobiles sold in America have been mandated to not only lower the emissions out the exhaust pipe, but also have to lower the total evaporative losses of gasoline from the entire car. A better sealing O-ring, with better barrier properties is critical to meeting these increased performance targets. The advantage of a nanotube-based O-ring is clearly shown in Table 3.

Table 3. Average Permeation Rate of 85% Fuel C / 15% Methanol after 28 days @ 23°C

Additive	Average Permeation Rate g*mm/m^2/day
Nanotubes	3.6
Carbon black	15.7

A surprising benefit of the use of nanotubes as the conductive additive is the change in resistivity with compression. Typically, as a conductive O-ring made with carbon black is compressed, the resistivity increases. It is thought that this is due to the breakage of the carbon black structure under compression. Table 4 shows how the nanotube-based formulation actually decreases in resistivity with compression. It is thought that the nanotubes are compressed closer together to increase conductivity but, because of their strength, do not break.

Table 4. Effect of Compression on Resistivity

Additive	Change in Resistivity With 10 Pounds Compression
Nanotubes	-292%
Carbon black	+224%

Performance of Nanotubes as a Flame Retardant (FR) for Plastics

All plastics are based on hydrocarbons and nearly all are combustible. The control of plastic's combustion with flame retardant (FR) additives is essential in many industries such as aircraft, building/construction, public transport, and electrical/electronics equipment.

FR additives work by breaking one of the links that produce and support combustion: heat, fuel and air. The control of the toxic byproducts and smoke is also becoming a factor in assessing flame retardant additives. Increasingly, FR additives are used in combination, often with a synergistic effect.

The search for non-halogenated FRs has led to nanoclays, one nm thick by 1000 nm. diameter. Initial research showed that the addition of as little as 5% of nano-sized clay particles could produce a 63% reduction in the flammability of nylon 6. More recent studies have shown that flame retardancy in many other polymers can be boosted by dispersing clay at the molecular level.

Two papers have been recently published on the use of multiwalled nanotubes as a flame retardant for plastics. G. Beyer [1] studied the effect of adding montmorillonite nanoclays modified with a quaternary ammonium compound and carbon multiwall nanotubes in ethylene-vinyl acetate (EVA).

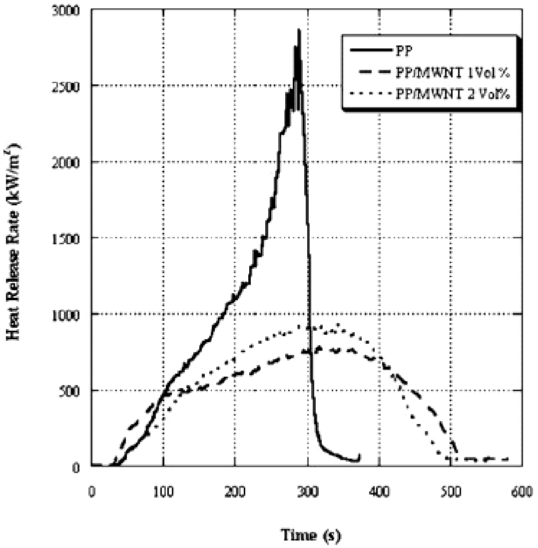
Beyer made several observations:

1. Nanotubes did not accelerate the time to ignition like the nanoclays (the clay's acceleration was attributed to the decomposition of the quaternary ammonium compound within the nanoclay.)
2. Nanotubes are better then nanoclays at reducing the peak heat release rate at either 2.4% or 4.8% loading. The char showed much lower crack density for nanotubes. The hypothesis is that the high aspect ratio of the nanotubes formed a reinforcing composite that made the char more resistant to cracking. The reduced cracking provided better insulation to the unburned polymer surface and hence reduced the emission of volatile gasses into the flame area.
3. An equal mixture of 2.4% nanotubes and 2.4% nanoclay gave a synergistic reduction in peak heat release rate. The char showed the least amount of cracking, due to the combined reinforcement effect of both fillers.

MWNT %	Nanoclay %	Time to Ignition sec	Peak Heat Release Rate kW/m2
0	0	84	580
2.4	0	85	520
4.8	0	83	405
0	2.4	70	530
0	4.8	67	470
2.4	2.4	71	370

Kashiwagi [2] studied multiwall nanotubes in polypropylene (PP). A comparison of heat release rate curves among the three samples is shown in Figure 5.

Figure 5. Heat Release Rate for PP with CMWNT



The results show that the heat release rates of the PP/MWNT nanocomposites are much lower than that of PP even though the amount of CMWNTs in PP is quite small. This reduction in heat release rate is at least as much as what was previously found for clay nanocomposites in a maleic anhydride modified PP. Kashiwagi attributed the performance of the MWNT more to the presence of the small amount of iron catalyst in the MWNT. This iron may form iron oxides during combustion and iron oxides have been used as FR additives.

Another possibility that has been suggested is that the nanotubes function by conducting heat away form the flame zone. It is obvious that much work needs to be done to understand the mechanism.

References

[1] G. Beyer, *Fire and Materials*, 26, (2002), 291-293.
[2] T. Kashiwagi, et.al., *Macromol. Rapid Commun*., 23, (2002), 761-765.